Clean-up of oat extracts for pesticide residues analysis by dSPE with PSA, C18, Z-sep or EMR-lipid, individually and combinations

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Clean-up of oat extracts for pesticide residues analysis by dSPE with PSA, C18, Z-sep or EMR-lipid, individually and combinations

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Introduction

The level of co-extracted matrix in QuEChERS cereal extracts (EN 15662) is generally high, but the highest levels are found in oat extracts due to the high fat content. Especially for oat flour stored at room temperature the matrix can result in poor method performance.
With the present study the EURL-CF wanted to elucidate whether an optimised clean-up procedure, employing more than one sorbent, could be suggested for oat flour stored 4 weeks at room temperature. Besides PSA (primary secondary amine) were Z-sep (zirconium based sorbent), EMR-lipid (enhanced matrix removal-lipid) and C18 found relevant to include in the study.

Study design

Oat extracts, un-cleaned or cleaned by dSPE with PSA, C18, Z-sep or EMR-lipid, were evaporated to dryness and the amount of matrix in mg/ml extract determined (Figure 1). GCMS chromatograms of these extract were obtained (Figure 2). A four factor 2-level factorial experiment (full resolution, 16 samples in double determination) was setup to study the effect dSPE clean-up with 16 different combinations of the four sorbents (Table 1) on the matrix level and analyte recoveries of 101 pesticides (spike level 0.02 mg/kg). Analyses of the final extracts were performed on GC-MS/MS.

Effect of PSA, C18, Z-sep and EMR-lipid on the levels of co-extracted oat matrix

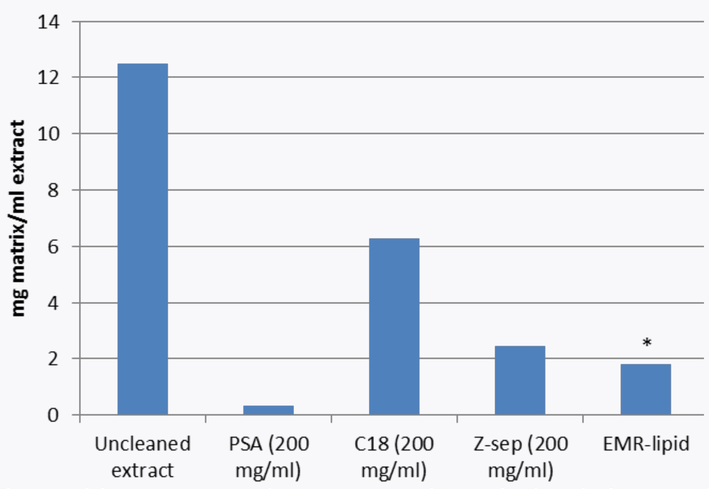

Figure 1: The residue amount of co-extracted matrix (mg/ml extract) measured after evaporation to dryness of oat extracts cleaned by dSPE with 200 mg of the individual sorbent per ml oat extract. Mean of double determinations except for EMR-lipid which was a single determination (market with an asterisk).

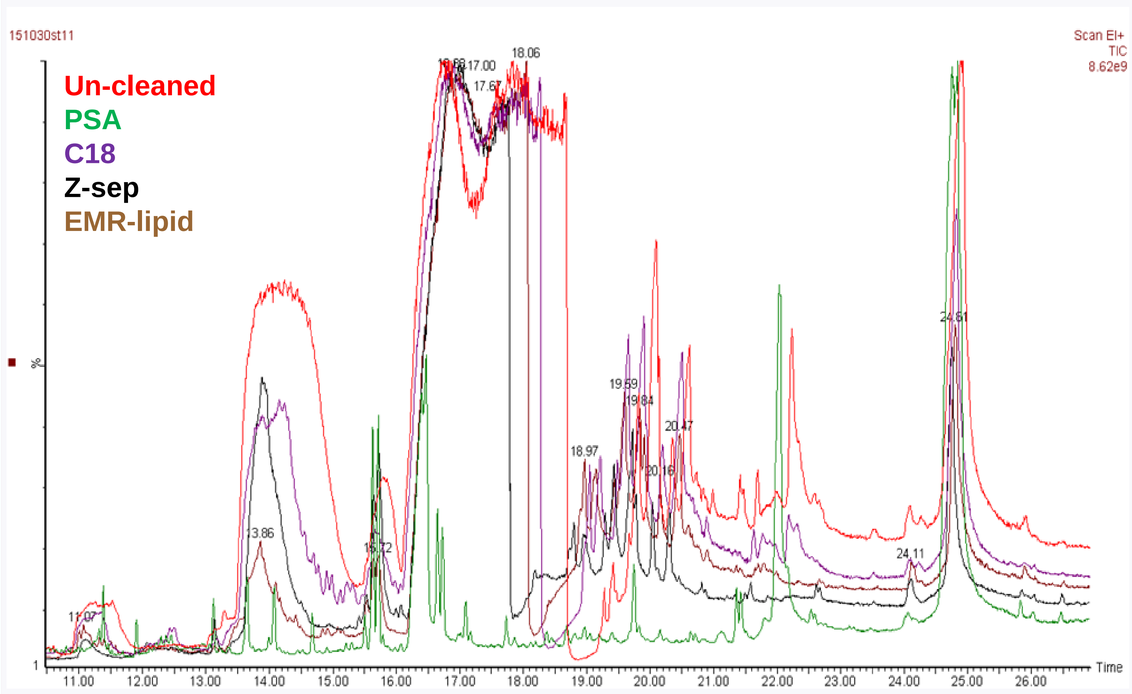

Figure 2: GCMS chromatogram of oat extracts after no cleanup or dSPE cleanup with PSA, C18, Z-sep (200 mg/ml) or EMR-lipid.

Factorial experiment - effect of various combinations of fours sorbents on analyte recovery and area of major matrix peak

Table 1: Design and results for the 2-level factorial experiment (full resolution).

Sample	PSA (mg/ml extract)	C18 (mg/ml extract)	Z-sep (mg/ml extract)	EMR-lipid	Analytes recov. 60-130%	Analytes w. recov. 60-150%	Major matrix peak (smallest (1) to largest (16)
1	0	0	0	0	41	53	16
2	150	0	150	0	68	81	7
3	150	150	150	EMR-lipid	42	44	3
4	0	150	0	0	39	51	15
5	0	150	0	EMR-lipid	53	60	11
6	150	0	0	EMR-lipid	65	76	8
7	**0**	**0**	**150**	**EMR-lipid**	**78**	**86**	**10**
8	0	0	150	0	37	53	14
9	0	150	150	0	39	60	13
10	150	0	0	0	42	69	5
11	0	150	150	EMR-lipid	51	54	1
12	150	150	150	0	75	78	4
13	**150**	**0**	**150**	**EMR-lipid**	**84**	**85**	**6**
14	150	150	0	0	71	85	2
15	0	0	0	EMR-lipid	48	71	12
16	150	150	0	EMR-lipid	42	45	9

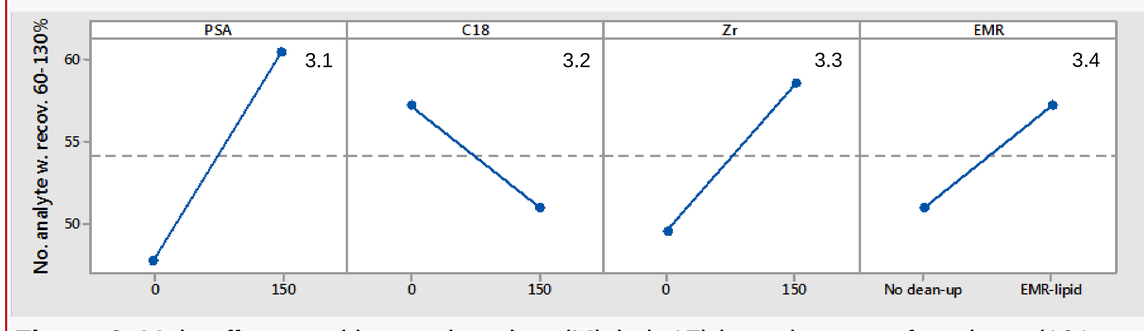

Figure 3: Main effects and interaction plots (Minitab 17) based on no. of analytes (101 in total) for which recoveries between 60-130% was obtained following the 16 different clean-up procedures. Zr: Z-sep.

QuEChERS validation – four dSPE procedures

Table 2: Percentage of 183 GC amenable pesticides that could be validated when using QuEChERS method with four different dSPE procedures corresponding to procedure 10, 13 and 7 in Table 1. Test material was oat spiked with 0.02 mg/kg (N=6 for each of dSPE method tested).

	Sorbents used in the dSPE procedure			
	25 mg PSA (EN 15662)	**150 mg PSA**	**150 mg of PSA and Z-sep+, EMR lipid**	**150 mg Z-sep+, EMR lipid**
Percentage of analyte validated (recov. 70-120 and RSDr<20)	87	89	80	85

Conclusion

All four sorbents were found to reduce the amount of co-extracted matrix in the oat extracts (Figure 1 and 2). Though, PSA had the most pronounced effect.

A factorial experiment showed that PSA, Z-sep as well as EMR-lipid increased the number of analytes for which acceptable recoveries were obtained (Table 1 and Figure 3.1, 3.3 and 3.4). Though PSA had again the most pronounced effect. C18 on the other hand reduced the number of analytes with acceptable recoveries (Figure 3.2). Procedure 10, 13 and 7 were chosen for validation study.

Very similar validation results were obtained when using dSPE according to EN15662 and the three selected dSPE procedures. Though for the EN15662 dSPE procedure shifts in retention times and distortion of peak shapes were observed for several compounds and data processing therefore became time consuming. Thus dSPE employing 150 mg PSA/ml of oat extract seems most appropriate for routine analysis.